The near-infrared nitric oxide nightglow in the upper atmosphere of Venus

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The v'=0 progressions of the $C \rightarrow X$ and $A \rightarrow X$ band systems of nitric oxide dominate the middle-UV spectrum of the night-time upper atmospheres of the Earth, Mars, and Venus. The $C(0) \rightarrow$ $A(0)+h\nu$ radiative transition at 1.224 μ m, the only channel effectively populating the A(0) level, must therefore occur also. There have been, however, no reported detections of the $C(0) \rightarrow A(0)$ band in the atmospheres of these or any other planets. We analyzed all available near-infrared limb observations of the darkside atmosphere of Venus by the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) instrument on the Venus Express spacecraft and found 2 unambiguous detections of this band at equatorial latitudes that seem to be associated with episodic events of highly enhanced nightglow emission. The discovery of the $C(0) \rightarrow A(0)$ band means observations in the 1.2–1.3 μ m region, which also contains the $a(0) \rightarrow X(0)$ emission band of molecular oxygen, can provide a wealth of information on the high-altitude chemistry and dynamics of the Venusian atmosphere.

The luminescence that results from exothermic chemical reactions between the constituents of a planetary atmosphere is customarily termed the night airglow or, simply, the nightglow (1). Although possibly present all day long, it appears most distinctly at night when the other processes of atomic and molecular excitation that depend directly on the action of the Sun are not at play and the diffuse radiation of solar light is at its minimum. The nightglow may originate from various, possibly minor, atmospheric constituents and provides insight into the chemistry, composition, temperature and energy balance of the atmosphere of a planet.

The $C^2\Pi \rightarrow X^2\hat{\Pi}$ and $A^2\Sigma^+ \rightarrow X^2\Pi$ band systems of nitric oxide (often referred to as the δ and γ bands, respectively) have long been known in the upper-atmospheric nightglow of the Earth (2, 3) and Venus (4, 5). More recently, they have also been reported in the atmosphere of Mars (6). A common structure, caused by the $\nu'=0$ progression of the aforementioned systems, characterizes the night-time middle-UV spectrum of all 3 planets. Separately and in combination with other nightglow emissions, observations of the nitric oxide nightglow have been used to infer details of the odd-nitrogen chemistry and dynamics in the emitting atmospheres.

In the dayglow, resonance scattering of solar photons from ground-state nitric oxide gives rise to additional $A \to X$ ($v' \ge 0$) bands that have been observed on the sunlit side of the Earth (7) but that remain undetected in the atmospheres of Mars and Venus. On Mars, and expectedly also on Venus, the emission of the $a^3\Pi \to X^1\Sigma$ system of carbon monoxide is likely to mask the nitric oxide $A \to X$ dayglow (8). The fluorescence efficiency of the C state is low for v = 0 and negligible for v > 0, presumably due to rapid predissociation (9–12). Day-time observations of the terrestrial atmosphere have found weak $C \to X$ (v' = 0) bands, which have been attributed to resonance scattering (13–15), although there are significant uncertainties (16).

Nitric Oxide Deactivation Branching Ratio

The C(0) level is readily formed by inverse predissociation in the laboratory recombination of unexcited nitrogen and oxygen

atoms (17, 18). The close match between laboratory spectra and nightglow spectra indicates that this is also the mechanism at work in the night-time upper atmosphere.

The $C(0) \rightarrow X(v'')$ progression constitutes 1 deactivation channel for the electronically excited molecule. The other important deactivation channel is $C(0) \rightarrow A(0)$, the production of A(v>0) being effectively precluded by Franck-Condon factor considerations (18). The subsequent $A(0) \rightarrow X(v'')$ progression, together with the $C(0) \rightarrow X(v'')$ progression, eventually lead to a hot vibrational population in the ground state of the molecule that may be detectable through its middle-infrared emission spectrum (19). At the low pressures in the nightglow region of the atmosphere, collisional quenching of C(0) and A(0) is very inefficient. In the absence of other effective production channels, the production of A(0) is therefore dictated by radiation from C(0). In turn, this implies that, in the nightglow, the emission rates for the $C(0) \rightarrow A(0)$ and $A(0) \rightarrow X(v'')$ transitions are the same, and that the ratio of the emission rate for $C(0) \rightarrow$ A(0) to the sum of the emission rates for $C(0) \to X(v'')$ and $C(0) \rightarrow A(0)$ is constant. Estimates of this branching ratio based on laboratory, theoretical, and observational investigations lie in the range 0.21-0.41 (9, 20-26). Some of these studies were adversely affected by contamination or by uncertain calibrations, so a consensus on a precise value has not yet been reached.

Our analysis of the spectrum of both UV progressions published recently (27) provides a new observational determination of the branching ratio. We digitized the published spectrum obtained by the spectroscopy for investigation of characteristics of the atmosphere of venus (SPICAV) instrument on Venus Express and fit it with synthetic spectra produced with the simulation software LIFBASE (28). The quality of the fit is very satisfactory, even for the weaker bands, as can be seen in Fig. 1. Our best fit leads to a branching ratio of 0.32.

Near-Infrared Nitric Oxide Band

Although laboratory experiments show that the $C(0) \to A(0)$ band should be present along with the $C(0) \to X(v'')$ and $A(0) \to X(v'')$ progressions, emission in the $C(0) \to A(0)$ band has never before been observed in the atmospheres of the Earth, Mars, Venus, or of any other planet. The $C(0) \to A(0)$ band comprises P, Q, and R main branches, with the lines of the stronger Q branch building up at $\approx 1.224~\mu m$ and those of the P and R branches spreading on either side toward longer and shorter wavelengths, respectively (30). At moderate to low spectral resolutions, however, the band spectrum looks more like a single line at the position of the Q branch (20, 31, 32).

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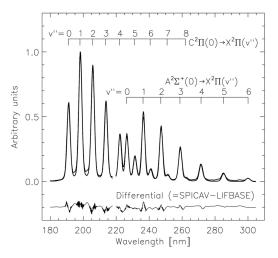


Fig. 1. Normalized SPICAV spectrum of the v'=0 progressions of the nitric oxide $C \rightarrow X$ and $A \rightarrow X$ nightglow on Venus (27) as digitized by us, and our best fit with a synthetic spectrum produced with LIFBASE (28) at a rotational temperature of 175 K. Both spectra are nearly undistinguishable on the scale of the plot. For the fitting, the observational spectrum is split near 220 nm, so that the 2 resulting partial spectra are allowed to shift in wavelength independently. The synthetic spectrum is defined by 4 free parameters: (i) the spectral resolution as given by the full width at half maximum, (ii) the Lorentzian component of the Voigt profile used in the convolution of the emission lines, and (iii and iv) the intensities of the 2 band systems. At the resolution of the spectrum, the choice of temperature within the plausible range 150-200 K (29) has no significant impact on the analysis. The best fit is obtained upon minimization of the integrated quadratic residual of the differential, i.e. observational minus synthetic, spectrum by means of a fully automated multivariate minimization algorithm. A best estimate of 0.32 is inferred for the ratio of the emission rate for $A(0) \rightarrow X(v')$ to the sum of the emission rates for $C(0) \rightarrow X(v')$ and $A(0) \rightarrow X(v')$. The emission rates for $A(0) \rightarrow X(v')$ X(v'') and $C(0) \rightarrow A(0)$ are equivalent for our situation. The bottom curve is the differential spectrum, and its small magnitude shows the good agreement between the observed and synthetic spectra. The high frequency fluctuations in the differential spectrum are artifacts from the digital rendering of the observed spectrum.

Estimates of the expected intensity of the $C(0) \rightarrow A(0)$ band on Venus may be derived from past and recent observations of the $C(0) \to X(v'')$ and $A(0) \to X(v'')$ progressions. The monochromatic nadir observations of the $C(0) \rightarrow X(1)$ band made by the Pioneer Venus Orbiter UV spectrometer (PVOUVS) found average vertical column intensities of 400 Rayleighs (R) over a 56°S-82°N/19:00-04:00 latitude/local time region, or 460 R over a reduced 60°S-66°N/20:00-02:00 region, with a particularly intense patch of \approx 1.9 kR centered at 10°S/02:00 (33, 34). (The Rayleigh is the conventional unit for airglow intensities. One Rayleigh represents the emission of 10⁶ photons per second from within a column of cross section 1 cm² into 4π sr) Using the intensity ratios provided by LIFBASE (28), these observations imply nadir intensities of 1.57, 1.80 and 7.45 kR for the entire v'=0 progression respectively. Further observations showed that on average the UV nitric oxide nightglow intensity peaks at ≈115 km and decreases with a scale height ≈3 km toward higher and lower altitudes (35). A nadir intensity of 1.5 kR for the $C(0) \rightarrow X(v'')$ progression implies a peak intensity for a limbviewing observation of ≈75 kR and a peak limb-viewing intensity of ≈ 35 kR for the $C(0) \rightarrow A(0)$ band. The latter assumes the branching ratio of 0.32 derived above.

The SPICAV instrument on Venus Express makes limb observations in the 180-300 nm region of the spectrum where the $C(0) \rightarrow X(v'')$ and $A(0) \rightarrow X(v'')$ progressions occur. A recent work (27) reported observations by SPICAV of the 2 UV progressions from a few selected orbits between January and September 2007 at 6.1°N to 71.8°N latitude. The observed vertical profiles of the line-of-sight integrated intensities for the 2 UV nightglow emissions show large variations in the altitude at which the emission peaks, 95-132 km. The average peak intensity summed over both progressions that they report is 32 kR, which implies the limb-viewing intensity of the $C(0) \rightarrow A(0)$ band should be ≈10 kR based on our inferred branching ratio of 0.32. These limb-viewing intensities are significantly smaller than those inferred above from the PVOUVS nadir observations. This difference is partly attributable to the reduced solar flux at the time of the SPICAV observations compared to the time of the PVOUVS observations, which reduces the rate of production of nitrogen and oxygen atoms on the day side. More importantly for the present work, the SPICAV observations also indicate that episodic events occur, especially at nearly equatorial latitudes, when the total UV nightglow exceeds 400 kR, possibly in response to dynamic events in the atmosphere. The identification of the $C(0) \rightarrow A(0)$ band in VIRTIS spectra should be comparatively simple in such an event.

Positioned on the shoulder of the $a(0) \rightarrow X(0)$ band of molecular oxygen, the detectability of the $C(0) \rightarrow A(0)$ band of nitric oxide in the VIRTIS spectra will be determined by its contrast against the typically stronger and highly variable oxygen emission. To aid our identification of the nitric oxide emission, we constructed a synthetic spectrum of the 6 spin-split P, Q, and R branches of the $C(0) \rightarrow A(0)$ band with the proper line positions (30), rotational energy levels (36) and line intensities (37). At the VIRTIS instrumental resolution of \approx 14 nm, approximately half of the total band intensity falls on the pixel that contains the Q branch. Consequently, a $C(0) \rightarrow A(0)$ limb intensity of 10 kR should appear in VIRTIS spectra as a 1-pixel prominence of $0.7 \times 10^{-4} \text{ Wm}^{-2} \text{ sr}^{-1} \mu\text{m}^{-1}$.

Detection of the Near-Infrared Nitric Oxide Nightglow

Descriptions of the Venus Express mission, the VIRTIS instrument and some initial results have been given elsewhere (38–40), and we refer the interested reader to those works for further details.

The VIRTIS archive of calibrated data up to April 2008 contains 25 orbits, which each have a sizeable number of spectra (\approx 150 or more) with exposure times of 8 s probing the limb of the planet at tangent altitudes of 112–118 km and local times of 20:00–04:00. These conditions provide the best opportunity for detecting the $C(0) \rightarrow A(0)$ band. Some of these orbits comprise multiple sessions during which the instrument observes continually and the observation data are stored to be subsequently transmitted back to Earth. In the mission nomenclature, the orbit is given by a 4-digit number, and the session is specified by 2 digits following the orbit number. The limb-viewing mode is operated near periapsis, which is near 75°N latitude for the highly eccentric orbit of Venus Express, so there is good coverage of the northern hemisphere but only limited access to the southern hemisphere. Eight of the 25 orbits show evidence of nightglow emission in the $C(0) \rightarrow A(0)$ band when altitudes near 110 km are probed. In all 8 cases, a narrow feature appears at the appropriate wavelength.

The only other molecule besides nitric oxide that could plausibly produce the observed emission is the hydroxyl radical. A few bands of its Meinel system with upper vibrational levels v' = 1-3 were in fact recently reported in VIRTIS data (40) at altitudes ≈95 km, significantly lower than those investigated here. The (7, 4) Meinel band has its origin near 1.21 μ m so emission in this band would appear at the same spectral position in VIRTIS observations as the $C(0) \rightarrow A(0)$ band of nitric oxide. Correspondingly, the (7, 5) Meinel band has its origin near 1.88 μm. Various theoretical calculations of the transition probabilities (41-44) indicate that the (7,5) band is 4 to 6 times as intense as the (7, 4) band. As a consequence, the absence of any

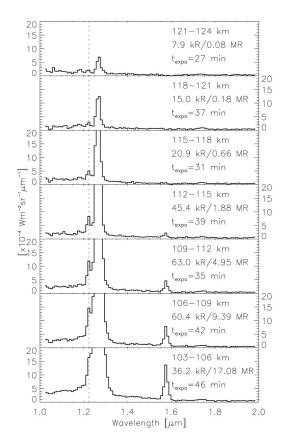


Fig. 2. Near-infrared spectra of session 0724_02 (14 April 2008). The position of the nitric oxide $C(0) \rightarrow A(0)$ band is indicated by the dashed line at 1.224 μ m. Estimates for the integrated limb intensity of the $C(0) \rightarrow A(0)$ band in kilo-Rayleighs were determined by removing the underlying molecular oxygen emission (see text). The stronger emissions centered at 1.27 and 1.58 μ m are the molecular oxygen $a(0) \rightarrow X(0)$ and $a(0) \rightarrow X(1)$ bands, respectively. Estimates for the integrated limb intensity of the $a(0) \rightarrow X(0)$ band are shown in MegaRayleighs. The estimated ratio of intensities of the 2 oxygen bands is 63 \pm 6 (40). In limb viewing, VIRTIS records tens to hundreds of time-sequences of slitwise-resolved spectra. Each spectrum is stored as an entry to a 2-index array. The equivalent exposure time, $t_{\rm expo}$, is evaluated from the number of entries added and the exposure time per spectrum (8 s), and gives a comparative measure of the signal-to-noise ratios in the spectra.

discernible feature at 1.88 μ m in the spectra under investigation rules out the possibility that we are seeing the Meinel system in emission at 1.22 μ m.

The spectrum from session 0724-02 (14 April 2008) in Fig. 2 shows our best example of the near-infrared nitric oxide nightglow in the upper atmosphere of Venus. The limb integrated intensity varies with altitude, reaching a peak somewhere between 109 and 112 km. The trend is consistent with the middle-UV nitric oxide nightglow, a consequence of the optical thinness of the atmosphere for all 3 nitric oxide emissions at these altitudes. Other features apparent in some of the plots are thermal emission from the lower atmosphere leaking through the clouds in the 1.10 and 1.18 μ m windows, and subsequently being scattered into the instrument and the $a(0) \rightarrow X(0)$ band of molecular oxygen at 1.27 μ m. On the scale of the figure, the thermal window at 1.74 μ m is barely discernible as a gentle undulation. The oxygen $a(0) \rightarrow X(1)$ band at 1.58 μ m is readily apparent below 115 km but is not detectable above.

Subtracting the underlying continuum by linear interpolation between the 2 neighbouring pixels, single-pixel radiances in the range $0.55 \times 10^{-4} - 4.41 \times 10^{-4} \, \mathrm{Wm}^{-2} \, \mathrm{sr}^{-1} \, \mu \mathrm{m}^{-1}$ are obtained for the altitudes quoted in Fig. 2, which translate, according to our

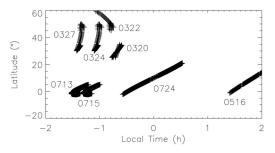


Fig. 3. Local time and latitude at the tangent point for the sessions referenced in the present work. The observations in orbits 0713 (3 April 2008) and 0715 (5 April 2008) used a new tracking system that allows for monitoring a fixed region of the atmosphere for a prolonged period.

earlier discussion, into limb intensities of 7.9–63 kR for the C(0)–A(0) band. At its peak, this implies a total intensity for the middle-UV nitric oxide nightglow of \approx 190 kR, significantly larger than the average value inferred by SPICAV but smaller than the 440 kR that SPICAV observed in orbit 0516 (27). It is clear that session 0724.02 is an episodic event of highly enhanced nightglow similar to those identified by SPICAV. Furthermore, by constructing altitude-averaged composite spectra for sequences of local time/latitude in the orbit, we can confirm that the nightglow is seen throughout the observation session, whose track on a local time/latitude map is displayed in Fig. 3.

Fig. 4 shows spectra from orbit 0516, in which the $C(0) \rightarrow A(0)$ band appears distinctly at somewhat lower altitudes than in orbit 0724. The inferred peak intensity in the UV is 108 kR, \approx 4 times less than previously reported for this very orbit at an unspecified location north of the equator (27). Factors such as the systematic averaging of individual spectra and the inevitably crude estimate of the $C(0) \rightarrow A(0)$ band intensities at our instrumental resolution may also contribute to the disparity between the SPICAV and VIRTIS findings.

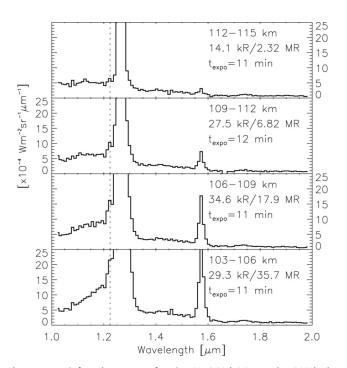


Fig. 4. Near-infrared spectrum of session 0516.02 (19 September 2007). The position of the $C(0) \rightarrow A(0)$ band is indicated by the dashed line at 1.224 μ m.

A feature at 1.22 μ m has also been identified for some latitude-altitude combinations in orbits 0320 (7 March 2007), 0322 (9 March 2007), 0327 (14 March 2007), 0713 (3 April 2008), and 0715 (5 April 2008), with estimated limb intensities \approx 10 kR. A somewhat stronger peak limb intensity, ≈20 kR, was observed between 30°N and 50°N in orbit 0324. We note that, in the 4 of these latter orbits which were before September 2007, SPICAV detected the nitric oxide nightglow in the middle UV.

Conclusion

We report 2 unambiguous detections of the nitric oxide $C(0) \rightarrow$ A(0) band nightglow at 1.224 μ m in the upper atmosphere of Venus during orbits 0516 and 0724. This is the first reported observation of this band in a planetary atmosphere. Its observation complements the $C(0) \rightarrow X(v'')$ and $A(0) \rightarrow X(v'')$ progressions previously observed in middle-UV spectra of the atmospheres of the Earth, Mars and Venus. The identification has been greatly facilitated by the occurrence of episodes of elevated nightglow emission at nearly equatorial latitudes. For the comparison with PVOUVS and SPICAV measurements, we determined a branching ratio of 0.32 for the ratio of the emission rate for $C(0) \rightarrow A(0)$ to the sum of the emission rates for $C(0) \rightarrow X(v'')$ and $C(0) \rightarrow A(0)$ from a middle-UV spectrum of the Venusian nightglow recently published. The information available from observations of the $C(0) \rightarrow A(0)$ band is the same

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as that available from the $C(0) \rightarrow X(v'')$ and $A(0) \rightarrow X(v'')$ bands but the $C(0) \rightarrow A(0)$ band intensity can be derived simultaneously with the intensity of the $a(0) \rightarrow X(0)$ band of molecular oxygen from VIRTIS limb observations.

The infrared spectrum of the night-time upper atmosphere of Venus is now known to be quite rich, with the nitric oxide and molecular oxygen nightglow occurring at its short-wavelength end. Both systems originate from the recombination of their constituent atoms, the nitric oxide nightglow through inverse predissociation and the molecular oxygen nightglow through 3-body recombination, but their emission rates peak at different altitudes. The nitrogen and oxygen atoms consumed in these recombination reactions are transported from the sunlit face of the planet, where they are produced, to the night side. It is obviously convenient to simultaneously monitor these 2 contiguous spectral features to help determine the mechanisms and rates of transport, in the horizontal and in the vertical, of the recombining atoms.

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